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(54) FLAME-RETARDANT COMPOSITION AND FLAME-RETARDANT ELECTRIC WIRE (57)Abstract:

PROBLEM TO BE SOLVED: To obtain a flame-retardant composition excellent in flame retardance and abrasion resistance and capable of readily coloring, and a flame-retardant wire. SOLUTION: This composition is obtained by adding 20-100 pts.wt. phosphate condensate and a nitrogen-containing organic compound to 100 pts.wt. polyethylene having ≥0.94 density and ≥5 ratio of weight average polymerization degree to number-average polymerization degree and the composition has ≥0.5 and <2 content of nitrogen and phosphorus. The flame-retardant wire is obtained by using this flame retardant composition as a coating material.

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CLAIMS

[Claim(s)]

[Claim 1] The fire-resistant constituent with which a consistency comes to add a phosphate condensate the 20 – 100 weight section and a nitrogen-containing organic compound or more by 0.94 as a flame retarder to the polyethylene 100 weight section whose ratio of a weight average degree of polymerization to a number average degree of polymerization is five or more, and is characterized by the ratios of nitrogen and the content of Lynn being 0.5 or more and less than 2.

[Claim 2] The fire-resistant constituent according to claim 1 characterized by being that to which a phosphate condensate uses ammonium polyphosphate as a principal component.

[Claim 3] The flame retardant cable characterized by using for pre-insulation and external covering the fire-resistant constituent shown in claim 1 or 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the flame retardant cable excellent in the abrasion resistance which used for pre-insulation and external covering the fire-resistant constituent used as covering material of the electric wire which needs the fire retardancy like for example, the electric wire for automobiles, and this fire-resistant constituent.

[0002]

[Description of the Prior Art] Fire retardancy is required while the electric wire used for industrial machines, such as transportation means, such as an automobile and a vessel, and an elevator, a robot, is excellent in abrasion resistance. As covering material of such [conventionally] an electric wire, the polyvinyl chloride resin constituent which blended the bulking agent, the plasticizer, and the stabilizer with polyvinyl chloride resin has mainly been used. However, since halogen content ingredients, such as such chlorine, generate the hydrogen halide gas of harmful nature by combustion and generate a lot of smoke, about the time of the outbreak of a fire, or abandonment processing, they do effect to the body or an environment and are posing a problem. Furthermore, recycling of the resource by ingredient recovery, heat recovery, etc. is desired about the covering material of these electric wires in the rise of an environmental problem.

[0003] However, especially the electric wire for automobiles has the electric wire very difficult for collecting and reusing the insulating material containing the polyvinyl chloride which only an electric wire is separated [polyvinyl chloride] at the time of dismantling of an automobile, and generates toxic gas since it wires intricately in a car body with which a thin line differs from die length. Actually, on the occasion of abandonment processing of an automobile, these electric wires are processed by incineration or reclamation in many cases. However, if a lot of polyvinyl chlorides are incinerated, the atmosphericair problem by hydrogen chloride gas will arise, and processing cost will become high. Moreover, even if it makes it processing by reclamation, cost is high, and continues to be continued and made today when the lack of land is aggravating. Moreover, securing a new reclamation lot leads to environmental destruction, and it will aggravate more.

[0004] On the other hand, about the cable and electric wire which are used for

a public building object etc., the flame retardant cable which hydrogen halide gas did not occur at the time of combustion, and used covering material with few yields of smoke has been conventionally developed from standpoints, such as disaster measures. As such covering material, the complex of an aluminum hydroxide, a magnesium hydroxide or a magnesium hydroxide, and a magnesium carbonate is blended with thermoplastics as shown, for example in JP,51–46341,A, and there is a constituent which added carbon impalpable powder further. Moreover, the hydrate of a compound and the constituent which added the red phosphorus system flame retarder are shown in polyolefine system resin at JP,57–92037,A. And these fire–resistant constituents are insulating materials which give fire retardancy to an electric wire and do not generate hydrogen halide gas at the time of combustion.

[Problem(s) to be Solved by the Invention] however, these fire-resistant constituents -- a conductor -- when it covered upwards and considered as the electric wire for automobiles, there is a possibility of wearing covering out remarkably and the above-mentioned fire-resistant constituent was inferior to the abrasion resistance required of the electric wire for automobiles with friction with the car-body body at the time of assembly, or components, and friction with the car-body body at the time of use, or other electric wires. [0006] Moreover, since carbon impalpable powder is added by the constituent shown in above-mentioned JP,51-46341,A, it is very difficult for the electric wire after covering to become black and to color by other colors. Furthermore, although coloring of a dark color can be performed since the red phosphorus system flame retarder is added by the constituent shown in JP,57-92037,A, light-colored coloring is very difficult. However, the above-mentioned constituent which needs to multiple-color-ize the narrow diameter electric wires the object for automobiles, the object for robots, for elevators, etc. for discernment, and contains carbon impalpable powder and a red phosphorus system flame retarder also from this point is unsuitable.

[Means for Solving the Problem] It is what offers an easy fire-resistant constituent and an easy flame retardant cable, the trouble above-mentioned [this invention] — canceling — fire retardancy and abrasion resistance — excelling — and coloring — the description As opposed to the polyethylene 100 weight section whose ratio [as opposed to a number average degree of polymerization in a consistency] of a weight average degree of polymerization is five or more or more in 0.94 It comes to add a phosphate condensate the 20 — 100 weight section and a nitrogen—containing organic compound as a flame retarder, and the ratio of nitrogen and the content of Lynn is in the flame retardant cable which used for covering 0.5 or more, the fire-resistant constituent it is [constituent] less than two, and this fire-resistant constituent.

[8000]

[Embodiment of the Invention] Its attention was paid to the polyethylene which is excellent in abrasion resistance as resin in order to raise the abrasion

resistance of a constituent. However, when additives, such as a flame retarder, do not have the consistency of polyethylene less than 0.94, sufficient abrasion resistance comes out, but since it is difficult to maintain abrasion resistance when additives, such as a flame retarder, enter, a consistency uses 0.94 or more polyethylene. In case this polyethylene performs extrusion molding, it tends to generate melt fracture, and extrusion molding cannot do the ratio of a number average degree of polymerization and a weight average degree of polymerization less than in five.

[0009] Moreover, in order to raise fire retardancy, many things were examined about the combination of the flame retarder of a white system, and the combination of the high phosphate condensate of fire-resistant effectiveness and a nitrogen-containing compound was chosen by little addition. Although polyphosphoric acid, sodium polyphosphate, potassium polyphosphate, ammonium polyphosphate, etc. were used, the meltable thing also usually raised whenever [condensation] to water as a phosphate condensate for a certain reason and the solubility to water is lowered, also in these, the condensate of ammonium phosphate is able to make whenever [condensation] high, and it is the hardest to melt to water and is effective.

[0010] However, in order to take out sufficient fire retardancy, it is insufficient and a nitrogen-containing organic compound is required only of a phosphate condensate. As a nitrogen-containing organic compound, a melamine system compound, a urea system compound, etc. may be added separately, and the phosphate condensate which added the nitrogen source may be used. Moreover, although description that fire-resistant effectiveness becomes high most was seen by reference when the ratio (N/P) of nitrogen and the content of Lynn was 2, this was mainly description to polypropylene and effectiveness was not enough to polyethylene. Then, as a result of examining various combination of N/P, it turned out that 0.5 or more and improvement fire-resistant by less than two are found for N/P, and N/P is preferably the most effective by 0.7 or more and 1.2 or less. In the combination of this flame retarder, if it needs to be added more than 20 weight sections and adds exceeding the 100 weight sections to the polyethylene 100 weight section on the other hand, although fire retardancy is maintainable, breaking strength and abrasion resistance will fall remarkably. [0011]

[Example] The compounding agent shown in Table 1 was elaborated by 10L kneader, it mixed at the temperature of 180 degrees C, and pellet processing was performed after that, the created pellet — 60phi extruder — the conductor of 0.5mm2 — it was upwards thick 0.3mm and extrusion covering was performed upwards. The sample offering sample was extracted from the electric wire after extrusion. In addition, extrusion temperature was considered as 200 degrees C of cylinder setup, and processing linear velocity was made into 300 m/min. The abrasion test fire retardancy sex test measured the electric wire in the condition that a conductor is in the interior. From the electric—wire sample, tensile strength created the tubing—like sample and performed it by the tension test (speed—of-testing 500 mm/min).

[0012] The evaluation approach is as follows. A result is shown in Table 1.

Abrasion resistance: JASO It carried out according to the blade round trip trial of the abrasion resistant test of D611, and 300 times or more were judged to be success.

Extrusion nature: With 60phi extruder, it judged by the feel of the appearance at the time of extruding by linear velocity 300 m/min, and the rough skin-like thing was made into the defect.

Tension test: JASO It carried out according to the insulator tension test of D611.

Horizontal-firing trial: JASO It carried out according to the fire-resistant trial of D611.

[0013]

[Table 1]

			上 收例								
ton i	1	2	3	4	5	1	2	3	4	5	6
PE-A	100	100	100	100	100				100	100	100
PE-B								100	- 100	1. 100	100
PE-C						100					
PE-D						147	100	 		 	
ま。リリン酸アンモニウム (E)	30		55		20	30	30	30	10	 	150
ポリリン酸アンモニウム(F)		30			20			30	10	10	150
ま。リリン酸ナトリウム			5	30	20			20			
メラミン				20				20		 	
耐摩耗性(回)	>1000	> 1000	390	420	700	30	000	646	50	1. 1.000	
押出加工性(外観)	良好	良好	良好	良好	良好		830 不良	940	460	>1000	210
強度(MPa)	21.5	20. 2	17. 6			良好		良好	良好	良好	良好
水平燃燒試験(燃燒時間)	10s	12s		18.0	20. 5	17. 4	18. 2	17.4	18-3	23. 4	8.2
N/P	0.57	128	8s	12s	3s	14s	12s	>]5s	>15s	>15s	3s
DE-4. Wm-7000 H140000		1.71	0, 52	1.47	1.14	0. 57	0. 57	0.34	11. 95	0.57	0. 57

PE-A:Mn=7000. Mw=140000、Mw/Mn=20, 密度=0.95 PE-B:Mn=10000, Mw=140000、Mw/Mn=14, 密度=0.96

[0014] The result of Table 1 shows the following thing.

An example 1 and example 1 of a comparison : Difference in the consistency of polyethylene. Abrasion resistance is bad when a consistency is low.

An example 1 and example 2 of a comparison: Difference in the ratio of the weight average degree of polymerization and number average degree of polymerization of polyethylene. An extrusion appearance has the bad one where a ratio is smaller.

Examples 1-5 and the examples 3 and 4 of a comparison: An optimum value is in nitrogen and the ratio of Lynn. Even if it is ineffective and exceeds 2, effectiveness is thin at less than 0.5.

Examples 1-5 and the examples 5 and 6 of a comparison: Reinforcement is inferior when many [when there are few additions which consist of a phosphate condensate and the nitrogen-containing organic substance, fire retardancy is bad, and].

[0015]

[Effect of the Invention] As explained above, the fire-resistant constituent of this invention is excellent in fire retardancy and abrasion resistance, and coloring nature is easy for it. Therefore, it is very effective when using as covering material, such as an electric wire for automobiles, an electric wire for elevators, and an electric wire for robots.

PE-C:Mn=20000, Nw=60000、Nw/Nn=3, 密度=0.92

PE-D: Mn=40000, Mw=110000、Mw/Mn=2.75, 密度=0.95

ま。リリン酸プンモニウム(E): 窒素16.5%, リン29.0%

ま。リリン酸アンモニウム(F): 窒素30%, リン17.5%

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(54) 【発明の名称】 難燃性組成物及び難燃性電線

(57)【要約】

【課題】 難燃性及び耐摩耗性にすぐれ、かつ着色容易な難燃性組成物及び難燃性電線を提供する。

【解決手段】 密度が 0.94以上で、数平均重合度に対する重量平均重合度の比が 5以上であるポリエチレン 100重量部に対し、難燃剤としてリン酸塩縮合物を 20~100重量部と含窒素有機化合物を添加してなり、窒素とリンの含有率が 0.5以上、2未満である難燃性組成物、及び該難燃性組成物を被覆材料に用いた難燃性電線、

【特許請求の範囲】

【請求項1】 密度が0.94以上で、数平均重合度に対する重量平均重合度の比が5以上であるポリエチレン100重量部に対し、難燃剤としてリン酸塩縮合物を20~100重量部と含窒素有機化合物を添加してなり、窒素とリンの含有率の比率が0.5以上、2未満であることを特徴とする難燃性組成物。

【請求項2】 リン酸塩縮合物がポリリン酸アンモニウムを主成分とするものであることを特徴とする請求項1 記載の難燃性組成物。

【請求項3】 請求項1又は2に示す難燃性組成物を絶縁被覆、外部被覆に用いたことを特徴とする難燃性電線。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、例えば自動車用電線の如き難燃性を必要とする電線の被覆材料として用いる難燃性組成物、及び該難燃性組成物を絶縁被覆、外部被覆に用いた耐摩耗性にすぐれた難燃性電線に関するものである。

[0002]

【従来の技術】自動車や船舶等の輸送手段やエレベータ、ロボット等の産業機械に用いられる電線は、耐摩耗性にすぐれるとともに難燃性が要求される。従来このような電線の被覆材料としては、ポリ塩化ビニル樹脂に充填剤、可塑剤、安定剤を配合したポリ塩化ビニル樹脂組成物が主に用いられてきた。ところが、このような塩素等のハロゲン含有材料は燃焼によって有害性のハロゲン化水素ガスを発生し、又多量の煙を発生するため、火災発生時や廃棄処理に関して、人体や環境へ影響を及ぼし問題となってきている。さらに、環境問題の高まりの中、これら電線の被覆材料について、材料回収、熱回収等による資源の再利用が望まれている。

【0003】しかしながら、特に自動車用電線は細線や長さの異なる電線が車体内に複雑に配線されているので、自動車の解体時に電線のみを分離し、有毒性ガスを発生させるポリ塩化ビニルを含む絶縁材料を回収して再利用することは非常に困難である。現実には、自動車の廃棄処理に際しては、これらの電線類は焼却又は埋立て等によって処理されることが多い。しかし、多量のポリ塩化ビニルが焼却されれば、塩化水素ガスによる大気問題が生じ、処理コストが高くなる。又埋立てによる処理にしても、土地不足が深刻化している今日コストが高く、今後も継続してできるものではない。又新規な埋立て用地を確保することは環境破壊につながり、より深刻化してくるだろう。

【0004】一方、公共建築物等に用いられるケーブル や電線については、従来、防災対策等の見地から、燃焼 時にハロゲン化水素ガスが発生せず、かつ煙の発生量の 少ない被覆材料を使用した難燃性電線が開発されてき た。このような被覆材料としては、例えば特開昭51-46341号公報に示されるような、熱可塑性樹脂に水酸化アルミニウム、水酸化マグネシウム又は水酸化マグネシウムと炭酸マグネシウムの複合体を配合し、さらに炭素微粉末を添加した組成物がある。又特開昭57-92037号公報にはポリオレフィン系樹脂に化合物の水和物と赤リン系難燃剤を添加した組成物が示されている。そして、これらの難燃性組成物は電線に難燃性を付与し、かつ燃焼時にハロゲン化水素ガスを発生しない絶縁材料である。

[0005]

【発明が解決しようとする課題】しかし、これらの難燃性組成物を導体上に被覆して自動車用電線とした場合、組立時の車体本体や部品との摩擦、使用時の車体本体や他の電線との摩擦によって、被覆が著しく摩耗するおそれがあり、上記難燃性組成物は自動車用電線に要求される耐摩耗性に劣っていた。

【0006】又上記特開昭51-46341号公報に示される組成物には炭素微粉末が添加されているので、被覆後の電線は黒色となり、他の色で着色することは非常に困難である。さらに、特開昭57-92037号公報に示される組成物には赤リン系難燃剤が添加されているので、濃色の着色は出来るが、淡色の着色は非常に困難である。しかし、自動車用、ロボット用、エレベータ用等の細径電線は識別のため多色化する必要があり、この点からも炭素微粉末、赤リン系難燃剤を含む上記組成物は不適当である。

[0007]

【課題を解決するための手段】本発明は上述の問題点を解消し、難燃性及び耐摩耗性にすぐれ、かつ着色容易な難燃性組成物及び難燃性電線を提供するもので、その特徴は、密度が 0.94以上で、数平均重合度に対する重量平均重合度の比が5以上であるポリエチレン100重量部に対し、難燃剤としてリン酸塩縮合物を20~100重量部と含窒素有機化合物を添加してなり、窒素とリンの含有率の比率が 0.5以上、2未満である難燃性組成物、及び該難燃性組成物を被覆に用いた難燃性電線にある。

[0008]

【発明の実施の形態】組成物の耐摩耗性を高めるため、 樹脂として耐摩耗性にすぐれるポリエチレンに着目し た。しかしながら、ポリエチレンの密度が 0.94未満 では難燃剤等添加剤がない場合は十分な耐摩耗性が出る が、難燃剤等添加剤が入ると耐摩耗性を維持することが 困難なため密度が 0.94以上のポリエチレンを用い る。このポリエチレンは押出成形を行う際にメルトフラ クチャーを発生し易く、数平均重合度と重量平均重合度 の比が 5未満では押出成形が出来ない。

【0009】又難燃性を高めるため白色系の難燃剤の組合せについて種々検討を行い、少量の添加で難燃効果の

高いリン酸塩縮合物と含窒素化合物の組合せを選択し た。リン酸塩縮合物としては、ポリリン酸、ポリリン酸 ナトリウム、ポリリン酸カリウム、ポリリン酸アンモニ ウム等が用いられ、水に可溶のものもあるため通常縮合 度を高めて水に対する溶解度を下げているが、これらの 中でもリン酸アンモニウムの縮合物が縮合度を高くする ことが可能で、水に対して最も溶け難く有効である。

【0010】しかし、十分な難燃性を出すためにはリン 酸塩縮合物のみでは不足で、含窒素有機化合物が必要で ある。含窒素有機化合物としてはメラミン系化合物、尿 素系化合物等を別途添加してもよく、窒素源を添加した リン酸塩縮合物を用いてもよい。又文献では窒素とリン の含有率の比率(N/P)が2の時、最も難燃性効果が 高くなるとの記述が見られるが、これは主にポリプロピ レンに対しての記述であり、ポリエチレンに対しては効 果が十分ではなかった。そこで、N/Pの組合せを種々 検討した結果、N/PがO.5以上、2未満で難燃性の 向上がみられ、好ましくはN/Pが0.7以上、1.2 以下で最も効果があることがわかった。この難燃剤の組 合せではポリエチレン100重量部に対し20重量部以 上の添加が必要であり、一方100重量部を超えて添加 すると、難燃性は維持できるものの破断強度、耐摩耗性 が著しく低下する。

[0011]

【実施例】表1に示す配合剤を10Lニーダーにて練り 上げ温度180℃で混合し、その後ペレット加工を行っ た。作成したペレットを600押出機により0.5mm ²の導体上に0.3mm肉厚で押出被覆を行った。供試 サンプルは押出後の電線より採取した。尚押出温度はシ リンダー設定200℃とし、加工線速は300m/mi nとした。摩耗試験難燃性試験は電線を導体が内部にあ る状態で測定した。引張強度は電線試料より管状のサン プルを作成して引張試験(引張速度500mm/mi n) で行った。

【0012】評価方法は次の通りである。結果を表1に 示す。

耐摩耗性 : JASO D611の耐摩耗性試験のプ レード往復試験に準じて行い、300回以上を合格と判 定した。

押出加工性 : 60 φ 押出機で、線速 300 m/m i n で押出した場合の外観の手触りにより判定し、鮫肌状の ものを、不良とした。

引張試験 : JASO D611の絶縁体引張試験に 準じて行った。

水平燃焼試験: JASO D611の難燃試験に準じて 行った。

[0013]

【表1】

実施例						比較例							
1	2	3	4	5		2		4	5	6			
100	100	_ 100	100	100				100		100			
							100	100	100	100			
					100		100						
					-112	100		_					
30		55		20	30		30	10	10	150			
	30						- 00		- 10	130			
		5	30				20	—					
			20	l				50					
>1000	>1000	390	420	700	30	830	940		> 1000	210			
良好	良好	良好.								良好			
21.5	20, 2												
10s	12s									8.2 3s			
0.57	1.71			1 11						0, 57			
	> 1000 食好 21. 5 10s 0. 57	100 100 100 30 30 30 30 5 5 5 5 5 5 5 5 5	2 3 100	100 100	100 100	100 100	100 100	1 2 3 4 5 1 2 3 100 1	1 2 3 4 5 1 2 3 4 100	1 2 3 4 5 1 2 3 4 5 1 100 1			

PE-A: Mn=7000、Nw=140000、Nw/Mn=20、密度=0.95 PE-B:Mn=10000, Nw=140000、Nw/Nn=14, 密度=0.96

PE-C:Mn=20000, Nw=60000、Nw/Mn=3, 密度=0.92

PE-D: Mn=40000, Mw=110000、Mw/Mn=2.75, 密度=0.95 す。月7酸7ンモニウム(E): 蜜素16,5%, リン29,0%

ポリリン酸アンモニウム(F):窒素30%, リン17.5%

【0014】表1の結果から次のことがわかる。

実施例1と比較例1 : ポリエチレンの密度の違

い。密度が低いと耐摩耗性が悪い。

実施例1と比較例2 : ポリエチレンの重量平均 重合度と数平均重合度の比の違い。比が小さい方が押出 外観が悪い。

実施例1~5と比較例3、4:窒素とリンの比率に最適 値がある。0. 5未満では効果がなく、2を超えても効 果がうすい。

実施例1~5と比較例5、6:リン酸塩縮合物と含窒素 有機物からなる添加量が少ないと難燃性が悪く、多いと 強度が劣る。

[0015]

【発明の効果】以上説明したように、本発明の難燃性組 成物は難燃性及び耐摩耗性にすぐれており、かつ着色性 が容易である。従って、自動車用電線、エレベータ用電 線、ロボット用電線等の被覆材料として用いるとき、き わめて効果的である。